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ENVIRONMENTALLY ACCEPTABLE ALTERNATIVES FOR NON-DESTRUCTIVE INSPECTION WITH FLUORESCENT PENETRANT DYES

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Current DoD handling and disposal costs associated with the nondestructive inspection (NDI) of metal parts (during manufacture and in-service) using fluorescent penetrant dye materials are estimated to be approximately $4 million per year. In an effort to minimize environmental impact, and reduce the handling and disposal costs associated with the use of current fluorescent dye penetrants, METSS has developed environmentally acceptable fluorescent dye penetrants for use with existing NDI techniques. METSS has utilized two specific bodies of background knowledge to support the program efforts: (1) previous efforts related to the development of non-toxic, environmentally friendly oils; and (2) previous efforts related to the development of non-toxic, environmentally friendly cleaners. Integration of this experience base into the program has resulted in the development of environmentally acceptable materials to support fluorescent dye penetrant NDI techniques in a time and cost effective manner.

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1.0 BACKGROUND

Nondestructive inspection techniques are routinely used during the manufacture and in-service evaluation of metal parts used in military applications to ensure the absence of critical defects. One of the most widely practiced inspection techniques is the use of fluorescent penetrant dye (FPD) materials. This process involves applying an oil-based penetrant containing a fluorescent dye to the surface under inspection. After a sufficient dwell time, during which the penetrant works its way into surface flaws, excess penetrant is removed from the surface with the aid of a cleaning agent. The cleaning agent is typically a product that emulsifies the oil carrier for easy removal. After the cleaner is applied, the surface is washed and dried prior to applying a developer. The purpose of the developer is to draw out the entrapped penetrant, thereby rendering visible the location and extent of any flaws in which the penetrant has become lodged. Oil-based penetrant fluid not only acts as a carrier solvent for oil-soluble fluorescent dyes, such as naphthalimides, rhodamines, and coumarin derivatives, but also ensures the fluorescent dye will not be readily removed during the application of the surface cleaning agent (emulsifier), thereby ensuring that any flaws are made visible upon inspection. Portable inspection kits used for field and flight line inspections consist of aerosol spray cans of dye, rinse and developer, and contain high VOC solvents that are used to remove the hydrocarbon penetrant fluid. Due to the number of steps involved in current FDP NDI techniques, the use of fluorescent penetrant dyes generate sizeable amounts of waste, including oily waste rags, which increases the handling and disposal costs associated with the use of this technique.

The DoD currently uses synthetic and petroleum based oils as carrier fluids for fluorescent dye penetrants for nondestructive inspection (NDI) of metal parts (during manufacture and in-service). Current DoD handling and disposal costs associated with these processes are estimated to be approximately $4 million per year. In an effort to minimize the environmental impact, and reduce the handling and disposal costs associated with the use of current dye penetrant NDI methods, the Strategic Environmental Research and Development Program (SERDP) is interested in the development of environmentally acceptable, non-hazardous materials that can be substituted in existing fluorescent penetrant dye practices.

2.0 TECHNICAL APPROACH

The technical approach taken to address the needs of the SEED program focuses on developing non-toxic, environmentally acceptable fluorescent dye penetrants and cleaning agents. METSS has drawn upon its extensive experience in developing environmentally friendly direct replacement fluid technologies to implement a practical approach to achieving the program goals. A core business of METSS is the development of environmentally friendly products and processes. Specifically, METSS has a proven track record conducting product development programs to identify or develop environmentally friendly *direct replacement* fluids for critical, high-tech applications. *Direct replacement* means these environmentally friendly alternative materials developed by METSS (1) meet the stringent physical property requirements of the existing fluids; (2) meet the in-service performance requirements of the current fluids; and (3) meet materials compatibility and handling requirements. Through a number of successful programs for industrial partners and the DoD, METSS has developed a range of environmentally benign, biodegradable direct replacement products for various applications, including:

- aircraft hydraulic fluids*
- dielectric fluids for sub-marine and underground power transmission cables*
- dielectric fluids for use in power transformers*
- corrosion inhibitors for aircraft hydraulic fluids, deicers and paints
- submarine hydraulic fluids*
- fiber-optic cable fill fluids*
- solvent emulsion cleaners
- deicers and anti-icers for aircraft, runway, roadway and agricultural applications
- soy-based dry film lubricants.*

***These environmentally friendly, biodegradable fluid development efforts were specifically aimed at direct replacement of non-biodegradable, toxic mineral oil/napthenic based fluids. Some of the products developed by METSS to support these high tech applications were actually derived from FDA approved food grade materials.**

As an integral part of these program development efforts, METSS has built industry-leading expertise in characterization of fluid biodegradability. METSS has become established as one of only a handful of facilities capable of accurately characterizing the degree of biodegradability of a given fluid in accordance with ASTM D5864 - *Standard Test Method for Determining Aerobic Aquatic Biodegradation of Lubricants or Their Components*.

METSS has drawn upon two specific bodies of background knowledge to support the current program efforts: (1) previous efforts related to the development of non-toxic, environmentally friendly oils; and (2) previous efforts related to the development of non-toxic, environmentally friendly cleaners. Integration of this experience base into the proposed tasks ensures the successful development of environmentally friendly materials to support fluorescent dye penetrant NDI techniques in a time and cost effective manner.

2.1 FLUID DEVELOPMENT PROCESS

The process used by METSS to develop environmentally friendly alternative materials can be broken down into four basics steps. A brief overview of these steps follows.

Technology Review. A review of the current technology is essential before starting a program of this nature. As METSS is heavily involved in the development of environmentally friendly fluid substitution technologies for DoD and commercial applications, METSS has a substantial knowledge base on the availability of existing technologies and the advantages and disadvantages of each of these systems. However, as with any new materials development program, the development of new fluorescent penetrant dyes is sure to have some specific requirements unique to the application. Thus, at the onset of the SERDP program, METSS conducted a technology review effort to establish a background and framework to compare and contrast the various state-of-the-art fluorescent dye penetrants used as inspection tools and to identify available technologies that could serve as alternatives to these systems. The intent of the technology assessment effort was to make sure METSS fully understood the application specific issues associated with fluorescent dye penetrants and the DoD and commercial needs in this regard.

Two major types of FPDs are used in military and commercial parts inspection operations: *Post-Emulsifiable (PE)* and *Water-Washable (WW)*. The PE FPD involves the application of a non-emulsifiable FPD to the part, followed by removal of the excess FPD from the surface with a water-based cleaner, followed by treatment with a developer. The WW FPD is applied in the same manner, but contains a high level of surfactants or emulsifiers that allow excess material to be washed from the surface with water alone. The most FPDs used are of the PE variety, and for this reason, METSS focused primarily on the development of the class of FPD. However, METSS also devoted a portion of the program efforts to the development on environmentally friendly WW FPDs as well as cleaning chemicals used as removers of the PE materials.

Raw Materials Selection. The initial step in the fluid development program is the selection of raw materials to serve as freezing point depressant basestocks. Materials selected must exhibit high water-solubility, low toxicity, and low biochemical and total oxygen demand (BOD and TOD). In addition, they must be relatively inexpensive and readily available. The materials selection criteria are purposely broad so as to include a large number of materials.

Testing and Evaluation. Once the potential raw material basestocks are selected, simple formulations were prepared and evaluated in a series of screening tests designed to evaluate some of the basic properties of these fluids, including flash point, viscosity, solubility, metal corrosion tendencies and FPD performance characteristics. Initial testing is defined so that a large number of materials or formulations can be screened efficiently and effectively. The results of the materials screening studies are used to eliminate candidate materials that demonstrate no potential for further development and to provide the information needed to direct subsequent formulation, reformulation, and optimization efforts. Frequently this involves the addition of minor fluid components such as corrosion inhibitors, antioxidants, and viscosity modifiers.

Down-Selection and Qualification Testing. The best overall fluid formulation from the testing and evaluation was targeted for qualification by independent or third party testing.

2.2 PERFORMANCE STANDARDS AND ACCEPTANCE CRITERIA

In the testing and evaluation phase of the program, METSS has relied primarily on the performance standards in the MIL-I-25135 and SAE AMS 2644C performance requirements, test methods and acceptance criteria for the various fluorescent dye penetrant formulations.

3.0 TECHNOLOGY REVIEW

METSS met with personnel from Magnaflux, the manufacturer of Zyglo® brand fluorescent dye penetrants, to review the current technology of fluorescent penetrant dyes. One of the goals of this meeting was to determine which fluorescent dye penetrant products were deemed to have the most significant environmental impact so METSS could target these in the initial formulation development efforts. Targeted products included ZL-27A and ZL-37 post-emulsifiable (PE) dyes as well as ZL-60D water-washable (WW) dye. The post-emulsifiable products contain little to no surfactant and are removed after application by a surfactant based cleaner. The water-washable products contain a surfactant system to allow them to be removed with water alone. Based on the composition of the fluids, METSS then identified three major formulation components of these products that were deemed less than desirable from an environmental impact standpoint and targeted these materials for replacement by more environmentally friendly alternatives (see Table 1).

Table 1. Hazardous FPD Components Targeted for Replacement

FPD Component	CAS Number	Comments
Severely Hydrotreated Naphthenic Petroleum Oils	64742-52-5	Naphthenic oils are considered non-biodegradable in the environment. Naphthenic oils appear on the Massachusetts Hazardous Substance List and have a rating of 1 by the International Agency for Research on Cancer (IARC). The IARC publishes monograph substances found to have at least sufficient evidence of carcinogenicity in animals.
Ethoxylated Nonylphenols	09016-45-9	Ethoxylated nonylphenol surfactants are not ultimately biodegradable; that is, they do not biodegrade completely to carbon dioxide and water. Instead, they breakdown to form phenols and phenolic derivatives, which are environmentally more hazardous than their precursors.
Phosphate Esters Isodecyl Diphenyl Phosphate Tributoxyethyl Phosphate	 29761-21-5 00078-51-3	Phosphate esters are generally listed as environmentally hazardous substances and marine pollutants due to their aquatic toxicity. The aromatic phosphate esters can also hydrolyze in water to form phenols and phenolic derivatives that are also environmentally hazardous.

During the technology review meeting, Magnaflux personnel demonstrated FPD application techniques used for crack determination and METSS personnel performed a few tests in order to become familiar with the tests procedures so they could be duplicated internally. METSS worked in concert with Magnaflux to characterize the performance of the materials used to support existing FDP NDI techniques. These efforts included identification of key properties of the FDP materials and the baseline performance data that was used to direct the program formulation development efforts. Particular emphasis was placed on product safety and handling issues (e.g., toxicity, flammability), along with the physical properties (e.g., viscosity, surface tension) and chemical properties (e.g., water and dye solubility, fluorescent properties) that affect product performance. Samples of ZL-60D water-washable (WW) dye as well as ZL-27A and ZL-37 post-emulsifiable (PE) dyes, ZR-10B Remover and ZP-9F Developer were obtained to support program efforts. Magnaflux also provided samples of the actual dyes used in the FPDs to support program development efforts.

4.0 MATERIALS SELECTION

METSS has accumulated a significant body of information and developed baseline physical property, toxicity and biodegradability data on a number of different environmentally friendly materials that can be used as replacement materials. From these efforts, METSS determined the following classes of materials to be of significance when environmental factors and toxicity are of concern in product formulation efforts:

Candidate Basestocks

- **Vegetable Oils.** The highly mono-saturated or high oleic vegetable oils (HOVO) and their methylated derivatives are non-toxic, food-grade materials with good solvency properties. They are also completely biodegradable and readily available a t a relatively low cost.
- **Polyalphaolefins (PAOs).** Low viscosity PAOs have been shown to be readily biodegradable and form these synthetic hydrocarbons basis of a new generation of high performance military hydraulic fluids. Additive solubility in PAO basestocks can be an issue, and other basestocks are often added to these fluids to improve solubility.
- **Cracked and Saturated White Oils (CSWO).** Low viscosity white mineral oils, another class of hydrocarbons widely used in food and pharmaceutical applications for their low toxicity, have also been found to be readily biodegradable. These materials also find use in specialty industrial applications. As with the PAOs, additive solubility can be an issue
- **Diesters.** Dibasic acid esters represent another class of materials of particular interest. These polar compounds provide excellent solvency and have been successfully substituted for more hazardous solvents in many industrial cleaning operations. The higher molecular weight diesters are often blended with PAOs to improve additive solubility in aircraft hydraulic fluid applications. Diesters are considered non-toxic and biodegradable.
- **Polyol Esters.** Polyol esters are widely used as substitutes for petroleum oils in environmentally sensitive applications. The are readily biodegradable and generally exhibit good solubility with additives.

Candidate Surfactants

- **Ethoxylated Linear Alcohols.** Linear alcohol ethoxylates are considered to be readily biodegradable and are replacing nonylphenol ethoxylates in environmentally sensitive applications at comparable performance with only a modest increase in cost.

- **Polyethyleneglycol (PEG) Esters of Vegetable Oils.** The vegetable derived PEG esters are completely biodegradable and are derived from renewable resources.

These basestocks and surfactants and blends thereof were used to formulate carrier fluids for the dyes. The basestock blends provide the proper solvency and viscosity required for a suitable FPD, while the surfactants provide the emulsification characteristics necessary to allow the excess FPD to be removed by the cleaner in the case of the PE fluids or water in the case of the WW fluids, while leaving enough FPD behind in the cracks to permit inspection.

In earlier research programs, METSS has performed biodegradability testing of various basestocks according to the method outlined in ASTM D5864 standard that considers the total degradation of the candidate fluids, including by-product degradation. By new standards, lubricants must *completely* breakdown through the action of living organisms into CO_2, H_2O, and energy to be considered biodegradable. Lubricants classified as *readily biodegradable* by this standard, biodegrade 60 to 100% in 10 to 28 days. As shown in Figure 1, synthetic esters and natural esters such as vegetable oils typically demonstrate greater than 80% biodegradability in 28 days. PAOs and CSWOs exhibit greater than 60% biodegradability. By comparison, the naphthenic oils only show about 10% biodegradability in the same 28-day test period.

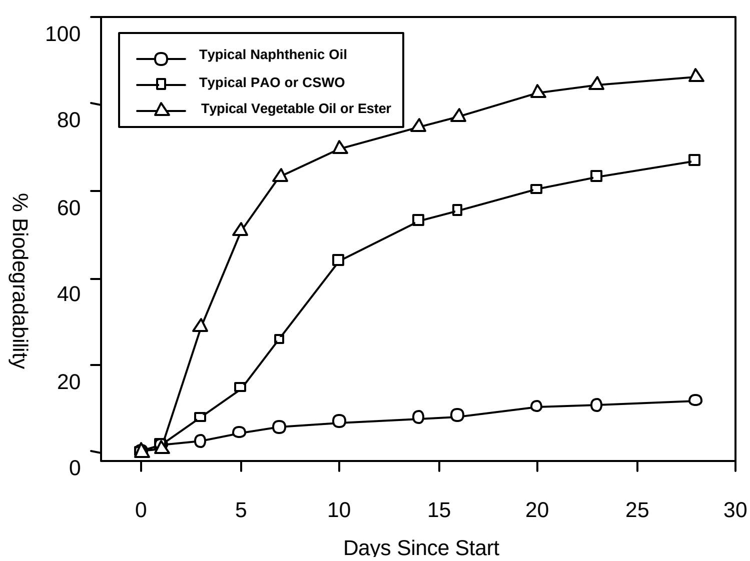


Figure 1. Biodegradability of Candidate Basestock Materials

5.0 EXPERIMENTAL METHODS

While the program effort is primarily focused on materials development, the program direction depended largely on the results of a well-defined strategy for testing and evaluating the candidate materials. The general physical and chemical requirements of the candidate materials have driven the initial materials selection and formulation efforts. However, formulation optimization has been driven by a screening protocol designed to evaluate material properties and performance in an effective and efficient manner. Testing and evaluation efforts performed under the program are discussed in this section. Detailed information on the testing and evaluation procedures can be found in the referenced documents.

5.1 FLASH AND FIRE POINTS (ASTM D93)

The flash and fire points of an organic liquid are basically measurements of flammability. The flash point is the minimum temperature at which sufficient liquid is vaporized to create a mixture of fuel and air that will burn if ignited. As the name of the test implies, combustion at this temperature is only of an instant's duration. The fire point, however, runs somewhat higher. It is the minimum temperature at which vapor is generated at a rate to sustain combustion.

5.2 VISCOSITY (ASTM D445)

Viscosity is a measure of a fluid's resistance to flow. The thicker the fluid, the higher is its viscosity and the greater its resistance to flow. Viscosity is measured by the *ASTM D445, Kinematic Viscosity* method. This test measures the amount of time required for a specified quantity of fluid, at a specified temperature, to pass through an orifice or constriction of specified dimensions. The thicker the fluid, the longer the time required for passage. Viscosity measurements of candidate fluids were conducted at 40^{o}C.

5.3 SOLUBILITY

Solubility was used as a simple test of mixture compatibility. Candidate formulations were prepared by adding the fluorescent dyes to the basestocks and allowing the blends to mix while heating (<60^{o}C) until the dyes dissolved. The samples were then placed in jars, allowed to cool to room temperature, and then visually observed over an extended time for signs of precipitation, crystallization or separation.

5.4 FREEZE-THAW STABILITY

Freeze-thaw testing was performed to determine the candidate fluids stability under exposure to alternating cold and warm environments. Candidate fluids were cooled to 0°F (-18°C) overnight, then allowed to warm to room temperature and observed for signs of separation, precipitation, crystallization or gelling.

5.5 PERFORMANCE TESTING

Modified methods of the *ASTM E 1209-99, Standard Test Method for Fluorescent Liquid Penetrant Examination Using the Water-Washable Process* and the *ASTM E 1210-99, Standard Test Method for Fluorescent Liquid Penetrant Examination Using the Hydrophilic Post-Emulsification Process* were followed to test the penetrant dye formulation candidates developed by METSS. The dye formulations were evaluated using an Eishin Type 1 Medium Crack Reference Panel. One reference panel cut in half was used for each trial. Side A was treated with the reference fluid, which corresponded to the comparable METSS formulation on side B of the panel.

5.6 UV-VISIBLE/FLUORESCENCE SPECTROSCOPY

UV-Visible and fluorescence spectroscopy was used to determine the UV-Visible absorption and fluorescence emission characteristics of existing dyes used in commercially available FPD formulations. Three separate components were characterized including: (1) fluorescent dye, (2) optical brightener #1, and (3) optical brightener #2. A concentration of 2.5 μM of each component was dissolved in methylene chloride. Methylene chloride solvent was used as the background for both UV-Visible and fluorescence measurements. The UV-Visible absorption spectra were obtained using a Carey Model 6 UV-Visible Spectrophotometer. Fluorescence emission spectra were obtained using a Photon Technologies International (PTI) research grade spectrophotometer. Instrument conditions included an excitation wavelength of 375 nm, excitation/emission monochrometer slit conditions of 1.25 μm, and a scan range of 385 – 600 nm. The excitation wavelength of 375 nm was selected due to the fact that most black lights used in NDI techniques have a primary emission in the range of 360-380 nm.

5.7 BRIGHTNESS MEASUREMENTS

The fluorescent brightness of existing and candidate FPD materials were evaluated using procedures adopted from *ASTM E1135-97, Standard Test Method for Comparing the Brightness of Fluorescent Penetrants.* Sample preparation consisted of saturating a 1 μm filter paper substrate with dye formulations diluted in methylene chloride at a volume ratio of 1:25 ml/ml. Three samples were prepared for each dye formulation. The dried filter paper substrate was then evaluated for fluorescence intensity using a PTI research grade spectrophotometer. The fluorescence intensity reported is the average of the three emission spectra obtained from the individual samples for any given dye formulation. Instrument conditions employed included an excitation wavelength of 365 nm, excitation/emission monochrometer slit conditions of 1.25 μm, a scan range of 375 – 600 nm, and an optical density filter (0.1% transmission) placed before the optical detector. All dye formulations were compared in intensity to Magnaflux's Zyglo ZL-37, a level 4, post-emulsifiable fluorescence penetrant dye formulation.

5.8 MODERATE TEMPERATURE CORROSION

The corrosive properties of the FPDs were evaluated on bare 7075-T6 aluminum alloy (AMS 4045), AZ-31B magnesium alloy (AMS 4377), and 4130 steel (AMS 6350). Each specimen was rinsed with acetone and blotted with an acetone soaked towel until clean and then allowed to air dry prior to corrosion testing. The specimens were placed in individual lass vials with screw caps. Each specimen was submerged no more than ¾ of its length with the test material (product formulation), capped, and placed in an oven at 50°C (+/- 2°C) for three (3) hours. At the end of the exposure period, the specimens were rinsed with deionized water, then acetone, and left to air dry. Once dry, the coupons were visually examined for evidence of pitting, tarnishing, etching, or corrosion. Acceptance criteria for deicing fluids are outlined in the SAE AMS 2466 specification.

6.0 FORMULATION DEVELOPMENT AND TESTING

Formulation development efforts were performed in an iterative manner, using the results of the testing and evaluation efforts to support performance optimization. As these efforts proceeded, the basic attributes of the materials used to support the formulation development efforts became increasingly important. Key aspects of the formulation development efforts are discussed in this section.

6.1 FLASH POINT

Flash and fire points are important properties of FPDs from a safety standpoint. The SAE AMS 2466 and MIL-I-25135 specifications require a flash point of not less than 200°F as measured by the ASTM D93 method. METSS reviewed flash data supplied by the manufacturers of the basestocks and surfactants and selected only those materials meeting this requirement as candidates.

6.2 SOLUBILITY AND FREEZE-THAW STABILITY

An important characteristic of the carrier fluids is their ability to solubilize the fluorescent dyes and hold them in solution without precipitation. METSS began initial formulation and screening efforts of the post-emulsifiable (PE) fluorescent penetrant dye by preparing blends containing the same level of fluorescent dye and optical brightener used in the current level 4 (most sensitive) FPD, and observing the samples for signs of separation. Freeze-thaw stability tests were conducted to accelerate the rate of sample aging and separation. It quickly became apparent that the dye and brightener compounds are more soluble in polar organic compounds, such as synthetic esters and vegetable oils, than in non-polar hydrocarbons such as polyalphaolefins and white mineral oils. For this reason, the formulation and development efforts focused on the esters and vegetable oils rather than hydrocarbons.

METSS formulated and tested for solubility and stability a total 54 post-emulsifiable (PE) FPDs, 6 water-washable (WW) FPDs and 1 remover. Following these initial screening tests, FPD candidates that remained soluble and stable were then evaluated for viscosity and performance characteristics.

6.3 VISCOSITY

Viscosity is an extremely important characteristic of fluorescent dye penetrants for several reasons. The fluid must be thin enough to flow into tiny cracks in order to facilitate their detection. However, fluids that are too thin are more easily removed by the cleaner, and will be washed out of the cracks, thereby

affecting inspection results. Fluids that are too viscous make removal of the excess FPD from the surface more difficult, and the surface residue interferes with inspection. Through proper basestock selection, it is possible to tailor the FPD formulation to the optimum viscosity. Table 2 compares the viscosities of the existing Magnaflux FPDs with those of candidate FPDs developed by METSS. Although the viscosities of the Magnaflux FPDs fall in the range of 10 - 14 centistokes at 40°C, METSS experimented with FPD viscosities over a broader range of 4 - 25 centistokes at 40°C in order to observe the effects on performance. While viscosity is expected have a major influence on performance, other factors such as basestock polarity can also affect the metal adhesion characteristics of the FPD, so the optimum viscosity could vary with the type of basestock used.

Table 2. Viscosity Comparison of Fluorescent Dye Penetrants and Removers

Post Emulsifiable FPDs	**Viscosity @ 40°C, cSt.**
Magnaflux ZL-27A	10.50
Magnaflux ZL-37	13.65
METSS PE-7	4.85
METSS PE-8	5.33
METSS PE-20	5.95
METSS PE-25	4.03
METSS PE-28	15.15
METSS PE-29	22.2
METSS PE-32	19.15
METSS PE-45	17.53
METSS PE-49	16.01
METSS PE-50	4.43
METSS PE-54	12.04
Water-Washable FPDs	**Viscosity @ 40°C, cSt.**
Magnaflux ZL-60D	11.11
METSS WW-3	15.14
METSS WW-6	17.85
PE FPD Removers	**Viscosity @ 40°C, cSt.**
Maganflux ZR-10B	45.69
METSS R-1	21.43

Viscosity is not expected to be as critical in the case of the removers, as these products are diluted with four parts water prior to use.

6.4 PERFORMANCE TESTING

Modified methods of the *ASTM E 1209-99, Standard Test Method for Fluorescent Liquid Penetrant Examination Using the Water-Washable Process* and the *ASTM E 1210-99, Standard Test Method for Fluorescent Liquid Penetrant Examination Using the Hydrophilic Post-Emulsification Process* were followed to test the penetrant dye formulation development process by METSS. The dye formulations were evaluated using paired Eishin Type 1 Medium Crack Reference Panels. Panel A or Side A was treated with a commercially available FPD product, either Zyglo ZL-27A, ZL-37, ZL-60D, or ZR-10B, and compared to Panel B or Side B which was treated with a comparable product formulated by METSS under the program.

The post-emulsification process provided a comparison of two separate penetrant dye formulations, the Level 3 ZL-27A and the Level 4 ZL-37, which exhibit two different levels of sensitivity. The two formulations follow the identical procedure for visually evaluating the penetration ability of the dye on the reference test panel. The test begins with a dwell time of 5 minutes to ensure that the dye has penetrated in to all the cracks of the reference panel. A pre-rinse of the reference panel was performed for 30 seconds before the emulsification of the dye. The test panel was placed into a bath with mild agitation; the bath contains a mixture of 20% ZR-10B Remover and 80% DI water, for 1 minute. The test panel had a final rinse for 30 seconds before being dried in an oven at 38ºC. A thin coat of ZP-9F developer was sprayed on the surface of the reference panel. In a darkroom, the test panel was illuminated with a Magnaflux ZB-100F black light. The final visual evaluation of the formulated penetrant dye was compared against its comparable Maganaflux penetrant dye and the reference template provided with the test panel.

METSS began work on post-emulsifiable fluids by developing PE formulations to compare with the Magnaflux ZL-27A Level 3 FPD, and later progressed to formulations comparable to the Magnaflux ZL-37 Level 4 FPD. Although the post-emulsifiable FPDs require the use of a cleaner to remove excess FPD from the surface, both the Magnaflux and METSS PE fluid formulations also contain a small amount of surfactant to assist in washing the excess FPD from the surface. METSS experimented with different viscosities and different levels of surfactant in the PE candidates. After some trial an error, several

candidate PE fluids were developed that provided comparable performance to the ZL-27A as shown in Table 3.

Table 3. PE Penetrant Dye Formulation Performance Compared Against the Magnaflux ZL-27A (Level 3 FPD)

Formulation	Visual Observations		
	Comparable	Non-Comparable	Comments
PE-25		X	All cracks visible, not as bright as ZL-27A
PE-26		X	All cracks visible, not as bright as ZL-27A
PE-27		X	All cracks visible, not as bright as ZL-27A
PE-28		X	All cracks visible, not as bright as ZL-27A
PE-32	X		All cracks visible, comparable to ZL-27A
PE-33	X		All cracks visible, comparable to ZL-27A
PE-34		X	All cracks visible, not as bright as ZL-27A
PE-35	X		All cracks visible, comparable to ZL-27A
PE-36	X		All cracks visible, comparable to ZL-27A
PE-37	X		All cracks visible, comparable to ZL-27A
PE-44		X	All cracks visible, not as bright as ZL-27A

Next, METSS began developing PE candidates to compare with the Magnaflux ZL-37 Level 4 FPD, which is much brighter in intensity than the ZL-27A fluid. After some conversations with Magnaflux, it was learned that the addition of a special brightener is required to achieve this intensity, and Magnaflux provided a sample of this material. METSS was able to successfully incorporate this brightener into the developmental PE fluids and achieve the same relative intensity as the ZL-37 product, but a difference in the color under the black light was observed. Some of these METSS PE fluids produced more of a greenish or bluish hue than the ZL-37, which had more of a yellow appearance. Some difficulties were also encountered in completely removing the excess PE FPD residue from the surface, but after some trial and error, comparable formulations were obtained as shown in Table 4.

Table 4. PE Penetrant Dye Formulation Performance Compared Against the Magnaflux ZL-37 (Level 4 FPD)

Formulation	Visual Observations		
	Comparable	Non-Comparable	Comments
PE-45	X		All cracks visible, comparable to ZL-37
PE-46		X	Slight white residue on surface of test panel
PE-47		X	Heavy white residue on surface of test panel
PE-48		X	Slight white residue on surface, not as bright as ZL-37
PE-49	X		All cracks visible, comparable to ZL-37, green color
PE-50	X		All cracks visible, comparable to ZL-37
PE-51		X	White residue on surface of test panel
PE-52		X	White residue on surface of test panel
PE-53		X	All cracks visible, not as bright as ZL-37
PE-54	X		All cracks visible, comparable to ZL-37

Although the PE fluids were the primary focus of the program effort, METSS did develop and evaluate a series of water-washable fluids as well. The test method for the water-washable penetrant dye formulations employed a dwell time of 5 minutes in the formulated penetrant dye. After several trials and different methods it was determined that the spray-off method provided an adequate rinse for the penetrant dye. A rinse time of 20 seconds was chosen because it provided the highest dye intensity when shown under the black light. The test panel was dried in an oven set at 38ºC and a thin coat of ZP-9F developer was sprayed on the surface of the dried panel. The test panel was illuminated in a darkroom with a Magnaflux ZB-100F black light. The final visual evaluation of the formulated penetrant dye was compared against Magnaflux ZL-60D penetrant dye and the reference template provided with the test panel. Test results are shown in Table 5.

Table 5. WW Penetrant Dye Formulation Performance Compared Against the Magnaflux ZL-60D (Level 3 FPD)

Formulation	Visual Observations		
	Comparable	Non-Comparable	Comments
WW-1	X		All cracks visible, comparable to ZL-60D, slight residue on surface
WW-2		X	Does not adequately wet surface of test panel
WW-3	X		All cracks visible, comparable to ZL-60D, slight residue on surface
WW-4		X	Dye residue remains on surface of test panel
WW-5		X	Dye residue remains on surface of test panel
WW-6	X		All cracks visible, comparable to ZL-60D

METSS also formulated an environmentally friendly remover formulation. This was a relatively simple task as it only involved the substitution of a biodegradable linear alcohol ethoxylate (LAE) in place of the nonylphenol ethoxylate (NPE) currently used. A great deal of information is available in the literature regarding this type of substitution in detergent formulations, and the comparable cleaning efficiency of LAE versus NPE is well documented. The evaluation of the METSS remover formulation followed the procedures described previously. The two Magnaflux dyes used in the post-emulsification, ZL-27A and ZL-37, were tested using the Magnaflux ZR-10B remover and the METSS formulated remover. As shown in Table 6, no differences were observed in the performance of the removers on the ZL-37 fluid. When tested with ZL-27A, the R-1 remover left a slight residue at the bottom of the test panel where it drains from the surface. Since METSS did not devote a great deal of time to the remover development, the minor differences observed cannot be considered statistically significant.

Table 6. Remover Formulation Performance Compared Against the Magnaflux ZR-10B (Remover)

Formulation	Visual Observations		
	Comparable	Non-Comparable	Comments
R-1 / ZL-27A		X	Cracks visible, residue remains on bottom of test panel
R-1 / ZL-37	X		All cracks visible, comparable to ZR-10B / ZL-37

6.5 UV-VISIBLE/FLUORESCENCE SPECTROSCOPY

The UV-Visible absorption and fluorescence emission spectra of the dye and optical brighteners used in the formulations are presented in Figures 2 through 4, respectively. The dye exhibited three discernable UV-Visible absorption peaks at 262, 279 and 428 nm, the peak at 428 nm being the only peak present in the "visible" region of the spectrum. Excitation of the dye at 375 nm resulted in fluorescence emission at approximately 482 nm. The primary dye emission at this excitation wavelength was relatively weak, compared to the fluorescence emission of both optical brighteners. The low fluorescence emission of the dye when excited at 375 nm is due to the minimal UV-Visible absorption that occurs at this excitation wavelength. However, when a dye formulation contains one of the optical brighteners, both of which emit relatively strongly at around 420 nm when excited at 375 nm, additional excitation energy is made available to the dye at a wavelength where strong absorption occurs. The presence of these optical brighteners would therefore enhance the fluorescence intensity (or brightness) of the fluorescent dye.

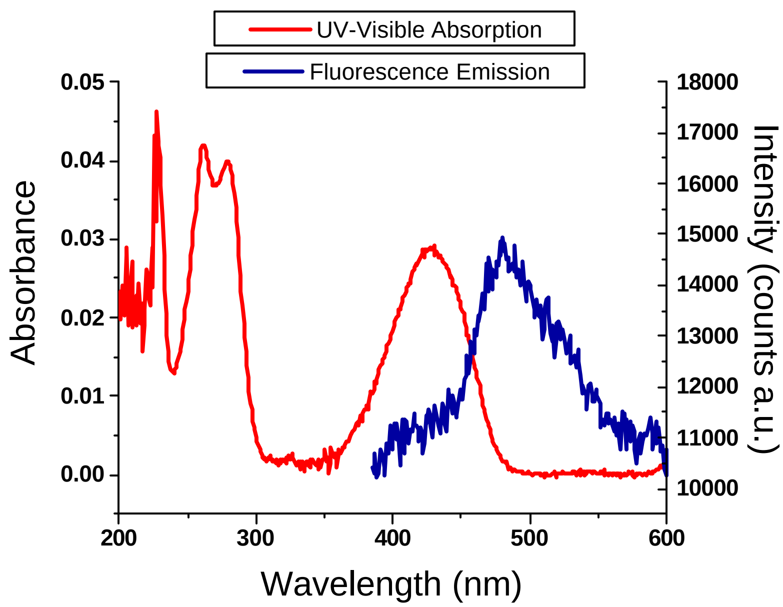


Figure 2. UV-Visible Absorption and Fluorescence Emission Spectra of Fluorescent Dye

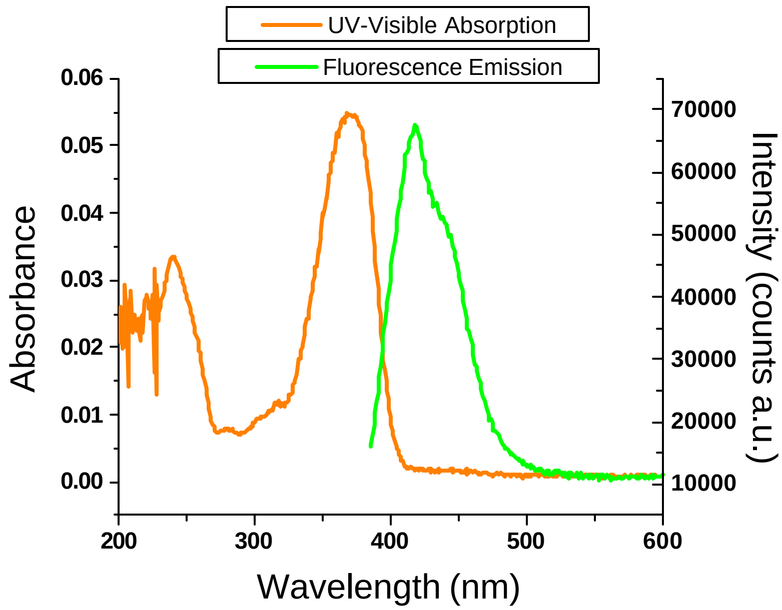


Figure 3. UV-Visible Absorption and Fluorescence Emission Spectra of Optical Brightener #1

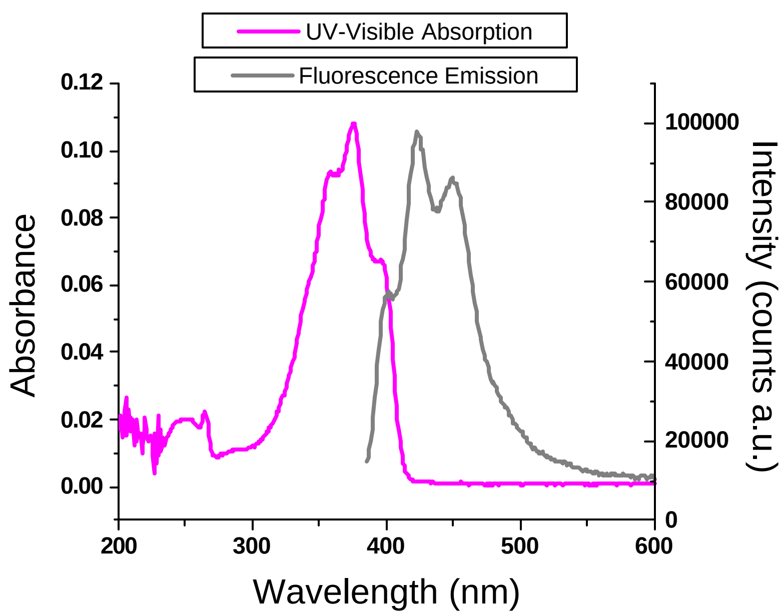


Figure 4. UV-Visible Absorption and Fluorescence Emission Spectra of Optical Brightener #2

6.6 BRIGHTNESS MEASUREMENTS

METSS measured the brightness of several candidate fluorescent penetrant dye formulations using a modified test protocol derived from *ASTM E1135-97, Standard Test Method for Comparing the Brightness of Fluorescent Penetrants.* The brightness measurements obtained were not color corrected to approximate the color response of the average human eye, but were instead measurements performed on a research grade instrument under controlled conditions to provide some quantitative measure of how intense (or bright) the fluorescence emission of the candidate fluorescent penetrant dye formulations was in comparison to commercially available, AMS-2644 compliant FPD materials, and specifically, Zyglo ZL-37.

The fluorescence emission spectra of the candidate FPD formulations evaluated are presented in Figure 5. The maximum fluorescence emission intensity of each FPD dye formulation was normalized with respect to the maximum fluorescence emission intensity for Magnaflux's Zyglo ZL-37 for comparison. These results are presented in Table 7. The brightness of the candidate FPD formulations ranged from approximately 65 to 87%, with METSS' PE-32 possessing the most intense fluorescence emission, achieving approximately 87% of that emitted by the Zyglo ZL-37 product. The reduced fluorescence emission intensity observed for METSS formulations PE-45 and PE-49 in comparison to the Zyglo ZL-37 FDP material were unexpected, as similar concentrations of each dye component were used in the preparation of these materials. A reduction in fluorescence emission can occur due to a variety of factors, including: decreased viscosity, increased temperature, increasing occurrence of quenching phenomenon, etc. METSS does not believe that polarity effects play a role in the reduced fluorescence emission, due to the fact that polarity effects are typically exhibited by a shift in the fluorescence emission wavelength. Further work will be required to increase the fluorescence emission intensity to levels comparable to those exhibited by commercially available FPD materials. This should be readily accomplished by increasing the concentration of dye and/or optical brightener(s) employed in the formulation.

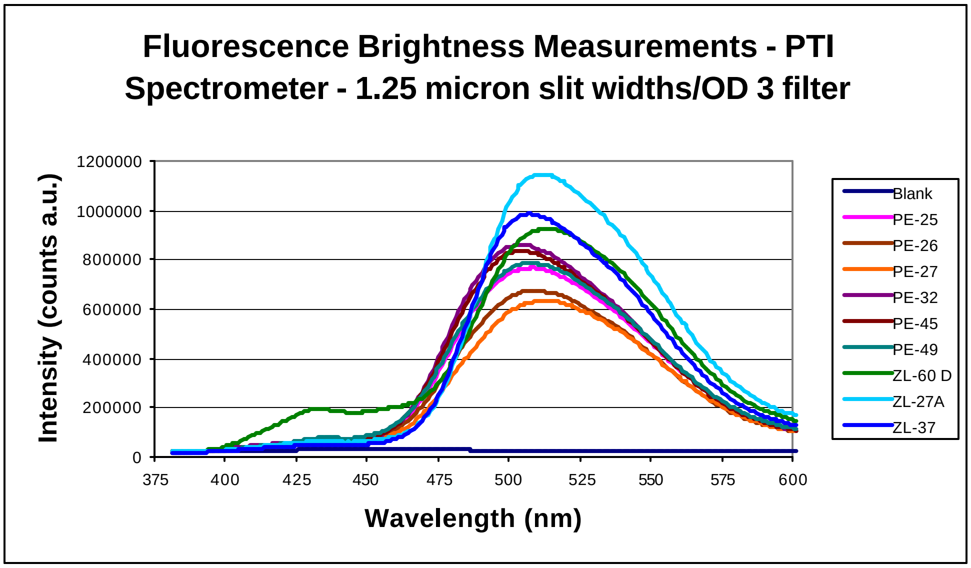


Figure 5. Fluorescence Emission Spectra of Candidate Dye Formulations for Brightness Measurements

Table 7. Fluorescent Brightness Evaluation of Candidate FPD Materials

Sample	Wavelength Maximum (nm)	Intensity Maximum (Counts, a.u.)	Brightness As Percentage of ZL-37 Intensity
Blank	469	28251	2.9
PE-25	504	756312	77.3
PE-26	509	666537	68.1
PE-27	510	627476	64.1
PE-32	503	851040	87.0
PE-45	504	827164	84.5
PE-49	506	778028	79.5
ZL-60D	513	918297	93.8
ZL-27A	511	1138507	116.3
ZL-37	506	978758	100.0

6.7 CORROSION TESTING

METSS evaluated the best candidate fluids for moderate temperature corrosion on common aircraft metals in accordance with the method outlined in SAE AMS 2466C specification for FPDs. Metals included bare 7075-T6 aluminum alloy (AMS 4045), AZ-31B magnesium alloy (AMS 4377), and 4130 steel (AMS 6350). Each specimen was rinsed with acetone and blotted with an acetone soaked towel until clean. The specimens were then allowed to air dry. The test specimens were placed in individual lass vials with screw caps. Each specimen is submerged no more than ¾ of its length with the test material, capped, and placed in an oven at 50°C (+/- 2°C) for three (3) hours. At the end of the exposure period, the specimens are rinsed with deionized water, then acetone, and left to air dry. Once dry, the coupons are visually examined for evidence of pitting, tarnishing, etching, or corrosion.

Corrosion test results are shown in Tables 8 – 11. None of the samples showed any signs of corrosion on the steel and aluminum specimens. Some of the magnesium coupons exposed to the developmental FPDs showed a slight discoloration, but this was only on one side of each affected coupon rather over the entire specimen. Surface consistency of the magnesium coupons may have had an influence on the test results. In earlier work conducted for the development of environmentally friendly aircraft deicing fluids, METSS observed inconsistent corrosion data on magnesium coupons that was traced to differences in surface preparation and treatment. It should be pointed out that none of the FPD formulations developed by METSS contained corrosion inhibitors, and no attempt was made to optimize the formulations for corrosion. This aspect of the environmentally friendly FPD should be addressed in any subsequent work.

Table 8. Corrosion Data for Magnaflux ZL-27A FPD and Comparable PE Formulations

Formulation	Metal	Coupon Appearance
ZL-27A	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change
PE-32	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change
PE-25	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change

Table 9. Corrosion Data for Magnaflux ZL-37 FPD and Comparable PE Formulations

Formulation	Metal	Coupon Appearance
ZL-37	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change
PE-45	AMS 6350 Steel	No change
	AMS 4377 Mg	Light discoloration on one side of coupon
	AMS 4045 Al	No change
PE-49	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change
PE-54	AMS 6350 Steel	No change
	AMS 4377 Mg	Light discoloration on one side of coupon
	AMS 4045 Al	No change

Table 10. Corrosion Data for Magnaflux ZL-60D FPD and Comparable WW Formulations

Formulation	Metal	Coupon Appearance
ZL-60D	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change
WW-3	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change
WW-6	AMS 6350 Steel	No change
	AMS 4377 Mg	Light discoloration on one side of coupon
	AMS 4045 Al	No change

Table 11. Corrosion Data for Magnaflux ZR-10B Remover and METSS R-1 Formulation

Formulation	Metal	Coupon Appearance
ZR-10B	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change
R-1	AMS 6350 Steel	No change
	AMS 4377 Mg	No change
	AMS 4045 Al	No change

6.8 DOWN-SELECTION AND EVALUATION BY MAGNAFLUX

Upon completion of the material development phase, METSS selected the best candidate formulations from each category of developmental fluids and submitted these materials to Magnaflux for evaluation in their laboratory. The materials provided included two post-emulsifiable fluids, one water-washable fluid and one remover. At the suggestion of Magnaflux, METSS provide the two best Level 4 PE candidates, rather one each of PE Level 3 and PE Level 4. FPDs of Level 4 sensitivity are the most difficult to achieve, and it was felt that this would provide a better measure of the performance capabilities of the new FPD candidates. The Magnaflux testing for fluorescent brightness indicated that the PE-45 and PE-54 FPDs fell just short of the minimum brightness requirement of 80% versus the standard. These fluids would easily meet the brightness requirements of a Level 3 FPD, however, and it was the opinion of Magnaflux that they could be improved to Level 4 sensitivity standards with minor modifications. The WW-6 FPD matched the standard for fluorescent brightness. A copy of the Magnaflux test report is provided as an Appendix to this report.

7.0 PROGRAM CONCLUSIONS AND RECOMMENDATIONS

From the tasks performed in the SERDP program METSS has clearly demonstrated the feasibility of developing new environmentally friendly technology for fluorescent dye penetrants. Tests performed by METSS, as well Magnaflux laboratories, have shown that the new FPDs should be capable of meeting the SAE AMS 2644C performance standards with only minor modifications required. The environmentally friendly FPDs developed by METSS under the SERDP program utilize biodegradable carrier fluids based on vegetable oils and their derivatives. These non-toxic materials, produced from renewable resources, are readily available, abundant and very cost effective. Significant cost benefits are likely to be the key driving force in pushing these materials into the existing fluorescent dye penetrant market. Based on METSS' preliminary estimates, a cost comparison with comparable products could lead to a savings of up to 20% a year in materials costs alone. Additional cost savings should be realized due to the reduced hazardous waste disposal costs associated with displacement of the current fluorescent penetrant dye materials.

METSS recommends that SERDP consider providing follow-on funding to fully develop the environmentally friendly FPD technology, as the program efforts identified several areas in need of additional work in order to qualify for the materials for general use. Testing by both METSS and Magnaflux indicates that additional formulation development efforts should focus on increased sensitivity and improved removability through optimization of the fluorescent dye blends and surfactant additive levels. The new FPDs may also require the addition of corrosion inhibitor additives not addressed in this program. Further development efforts should also investigate the potential use of alternative dye components that are highly biodegradable, in addition to the carrier fluids addressed by the current program.

APPENDIX

MAGNAFLUX TEST REPORT

MAGNAFLUX®
A Division of Illinois Tool Works Inc.

July 24, 2003

Bradley L. Grunden, Ph.D.
METSS Corporation
300 Westdale Avenue
Westerville, OH 53082

Dear Mr. Grunden:

We have evaluated the materials that you submitted. Below are the results that we observed.

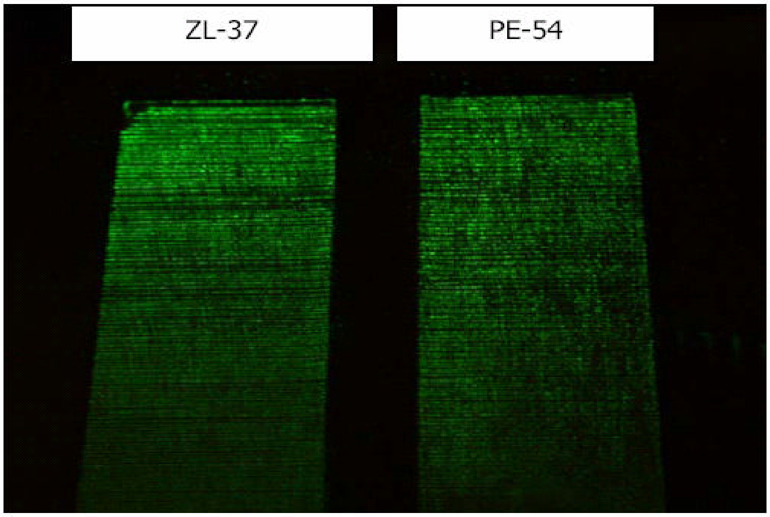
Test	PE-45/R-1	PE-54/R-1	WW-6
Viscosity Kinemtic, 200 cannon-feske tube	28.80cs	11.94cs	19.17cs
Fluorescent Brightness	67.94% (ZL-37 std)	73.07% (ZL-37 std)	100% (ZL-67 std)
Removability	Not equal	Not equal	Not equal

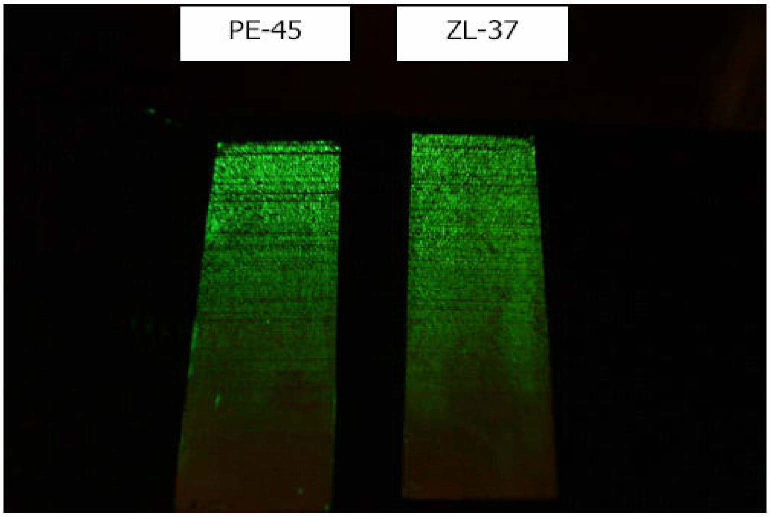
The viscosity of typical PE penetrants is less than 10 cs however PE-54 and PE-45 were able to penetrate the test panels in the 10 minute required dwell time.

PE-54 and PE-45 did not pass the brightness test. They were tested against ZL-37 which is a level 4 PE penetrant. The minimum is 80% of standard. The WW-6 passed at 100% of standard which is what is typically seen for ZL-56 (Level 4 WW).

The removability test was done by placing penetrant on a sand-blasted aluminum panel for 5 minutes followed by a 30 second rinse and a one minute remover dwell (20% solution) and a 30 second final rinse. The panels are dried in a 130°F oven for 5 minutes and developed using ZP-4B Dry Powder Developer. The panels are then compared to a standard processed using the same parameters. The result must be equal to or better than the standard. In the case of PE-45, PE-54, and WW-6 they did not perform as well as the standard. It was noted that the PE-54, PE-45, and WW-6 panels showed a blue fluorescent background whereas the standard did not have the blue fluorescent background.

The sensitivity test was done using Ni-Cr tapered panels. I have attached some photos of the PE-54 and PE-45 sensitivity panels. Due to technical difficulties I was unable to photograph the WW-6 evaluation. The overall results of the sensitivity tests showed the three penetrants are very close but not equal to the standards. The PE-45 performed better than PE-54.





MAGNAFLUX®
A Division of Illinois Tool Works Inc.

In conclusion, I feel the penetrant formulations are very close. With a few minor adjustments these formulations could be successfully used in NDT applications.

Please let me know if you have any questions or comments. I have enjoyed our conversations and I am looking forward to next phase of this project.

Sincerely,

Tamie Simmons

Tamie Simmons
Research Manager
Magnaflux